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Investigations Involving Galvanic Cells with the Solid $Zr_{0.85}Ca_{0.15}O_{1.85}$ Electrolyte

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Scientists in the Metallurgy and Ceramics Research Laboratory at the ARL are interested in the development of improved techniques for the determination of thermodynamic data (e. g. the free energy change associated with certain types of chemical reactions). Calculations using such thermodynamic data can often predict whether or not chemical reactions will occur at high temperatures.

One of the most advantageous methods used in the determination of thermodynamic data is the galvanic cell technique. A galvanic cell is a device used to convert chemical energy into electrical energy. The open circuit voltage produced by the galvanic cell is a measure of the thermodynamic free energy which is potentially available from the chemical reaction of the cell.

In 1933, Professor Carl Wagner derived theoretically the following equation for the electromotive force E of a galvanic cell involving a crystalline chemical compound of the type $Me_{Z_2}X_{Z_1}$ as the electrolyte.

$$E = -\frac{1}{F}\int_{\mu'_{Me}}^{\mu''_{Me}} (t_1+t_2)\,\frac{d\mu_{Me}}{|Z_1|} = -\frac{1}{F}\int_{\mu'_{X}}^{\mu''_{X}} (t_1+t_2)\,\frac{d\mu_{X}}{|Z_2|}$$

where F is Faraday's constant, t_1 and t_2 are the fractions of current carried (transport numbers) by the cations (positive ions) and anions (negative ions), respectively, of the $Me_{Z_2}X_{Z_1}$ electrolyte, Z_1 and Z_2 are the valences, and μ_{Me} and μ_X the chemical potentials of the metal

and non-metal, respectively. The cathode and anode of the cell are indicated by (') and (''), respectively. In recent years, Eq. (1) has become the basis for the use of solid crystalline electrolytes in the galvanic cell technique, since it relates the voltage E of a cell to the free energy change associated with the virtual chemical reaction of the cell.

Galvanic cells using the crystalline electrolyte $Zr_{0.85}Ca_{0.15}O_{1.85}$ have shown great promise in the investigation of the thermodynamics of oxides. This electrolyte was introduced by Kiukkola and Wagner 1957. Since then it has been used increasingly in high temperature fuel cells, for the determination of the free energies of formation of binary and ternary oxides, and for the determination of activities in alloys. However, as seen in Eq. (1), the voltage of a galvanic cell will correspond exactly to the free energy change for the chemical reaction of the cell only if $t_1 + t_2 = 1$, or, in other words, if the entire current in the electrolyte is carried by ions and the electronic fraction of the current is negligible. The temperature range over which this necessary condition is satisfied by the high-temperature electrolyte $Zr_{0.85}Ca_{0.15}O_{1.85}$ had not been determined until Drs. Vest, Tallan, and Rapp attacked the problem.

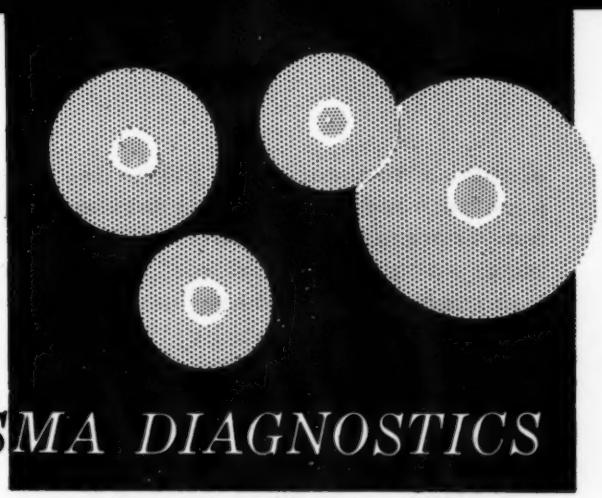
At a constant oxygen pressure of 10^{-9} atmosphere, the ionic transport number (t_1+t_2) for $Zr_{0.85}Ca_{0.15}O_{1.85}$ was measured by two complimentary techniques. First, the dc voltage necessary to maintain a constant current of the order of 1 to 10 microamperes was measured as a function of time. A dc voltage applied across an ionic-conducting crystal will polarize the crystal, i. e. set up an ionic concentration gradient due to a potential-driven ionic diffusion. As polarization increases, a higher voltage is continuously demanded to maintain a constant current. By substituting the experimental data into a mathematical expression describing the polarization phenomenon, the ionic transport number was calculated over a range of temperatures. The ionic transport number $(t_1 + t_2)$ for $Zr_{0.85}Ca_{0.15}O_{1.85}$ had the following values: 0.999 at 700°C, 0.997 at 600°C, 0.978 at 505°C, 0.857 at 413°C, and 0.752 at 312°C.

In addition to these polarization measurements, the total conductivity (ionic and electronic) of $Zr_{0.85}Ca_{0.15}O_{1.85}$ was determined by measuring the current passing through the sample with a high-frequency ac voltage applied. Under this condition the sample does not polarize. A plot of the logarithm of the total conductivity vs 1/T revealed high temperature and low temperature linear portions. The slope of the high temperature ($T > 600°C$) straight line corresponded to the activation energy for the diffusion of oxygen ions in $Zr_{0.85}Ca_{0.15}O_{1.85}$ as measured independently by other authors, proving that oxygen ion conductivity is dominant above 600°C. At low temperatures the electronic conductivity becomes significant. Transport numbers calculated from ac conductivity data agreed very well with those determined by the polarization technique.

In summary, the results indicate that $Zr_{0.85}Ca_{0.15}O_{1.85}$ exhibits essentially pure oxygen anion conduction ($t_2 = 1$) at temperatures above 600°C for an oxygen partial pressure of 10^{-9} atmosphere. Thus, Eq. (1) may be used without significant error to describe galvanic cells empldying this electrolyte above 600°C. At lower temperatures, mixed electronic and ionic conduction are present and Eq. (1) cannot be used without introducing appreciable error.

Future investigations are planned which will determine the ionic transport number in this material as a function of oxygen partial pressure. Theory predicts that excessive electronic conductivity may be present at very low oxygen pressures.

GUARD RING PROBES in PLASMA DIAGNOSTICS



RICHARD S. PALMER, Plasma Physics Research Laboratory (ARL)

For many years the Langmuir probe method has been a powerful technique in measuring plasma parameters such as space potential, electron concentration, and electron temperature. Langmuir's method consisted of determining the complete voltage-current characteristic of a small auxiliary electrode (probe) of standard shape placed in the path of a glow discharge. In this way Langmuir found it possible to accurately determine the potential of the space near the probe and to obtain much information concerning the nature, velocity, and space density of the discharge particles. Using this technique, Langmuir and co-workers expanded the theory of probes and their surrounding sheaths to encompass many types of probe geometries and discharge conditions.

The essential but difficult problem with any probe measurement is the correct and inclusive interpretation of the probe voltage-current characteristic taking into account the discharge conditions and the probe geometry. Probe curves may be falsified by many factors. Among these are the disturbance of the discharge by the probe, the changing conditions at the probe surface, discharge oscillations and the complicated behaviour of the probe sheath for a standard type probe.

To obtain a better understanding of the sheath effects surrounding a standard Langmuir plane probe, a research group in the Plasma Physics Research Laboratory has undertaken a series of experiments, one being the guard ring probe, under conditions which minimize undesirable disturbances in the discharge.

To obtain a more uniform plane sheath geometry which is

adaptable to theory, the probe design shown in Figure 1 has been adopted. A plane probe is formed by the flat end of a 0.5 mm diameter molybdenum or kovar wire. The wire is surrounded by a molybdenum, kovar, or platinum cylinder whose annular end face forms the concentric guard ring. A deep, narrow (125 microns) cylindrical gap separates the wire from the metal cylinder. In this way the probe is insulated from the guard ring without using a dielectric insulator which would collect a negative surface charge and disturb the field of the guard ring probe. The outer surface of the metal cylinder is coated with alumina. Separate leads to the probe and guard ring allow their potentials to be varied independently if required.

The voltage-current characteristic of this guard ring probe is being investigated in a hot cathode discharge in argon at pressures up to a few mms of mercury. A barium oxide coated cathode and a hollow anode are used to minimize plasma oscillations or column striations.

The probe is cleaned by positive ion bombardment before each run. The voltage applied to the probe is swept using a triangular function generator. The probe voltage and resulting current are displayed on an oscilloscope and photographed during each run.

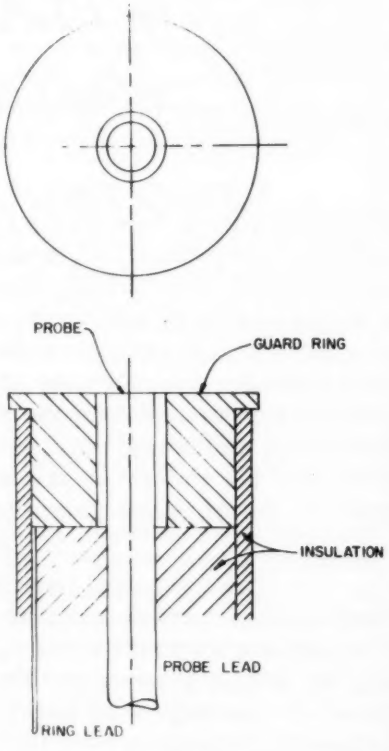


Fig. 1 - GUARD RING PROBE

The guard ring probe has already proved useful. Initial measurements and photographs of the probe ion current show that the guard ring probe, with shield and probe at the same potential, appears to correct for the sheath edge effects of a standard Langmuir probe in the ion collecting region of the characteristic. An edge correction given by Langmuir was applied to the standard Langmuir probe curve; Figure 2a shows that the resultant curve agrees well with the curve obtained directly using the guard ring probe.

The measurements have been extended into the electron

collecting region. The curves obtained are of the form shown in Figure 2b. The experiments are being continued with the aim of interpreting the influence of the sheath fields on probe electron collection.

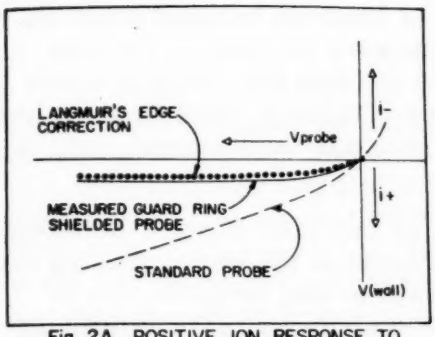


Fig. 2A POSITIVE ION RESPONSE TO GUARD RING SHIELDED PROBES

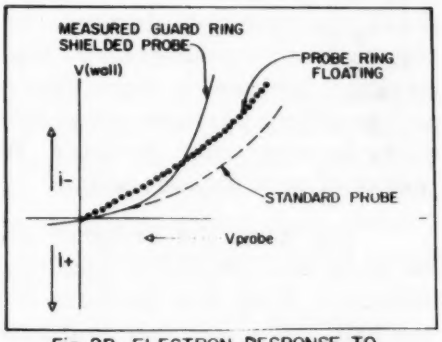
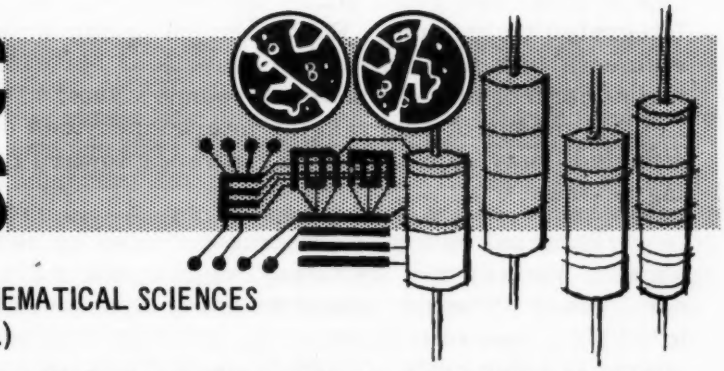


Fig. 2B ELECTRON RESPONSE TO GUARD RING SHIELDED PROBES

synthetic networks



COMPUTER AND MATHEMATICAL SCIENCES LABORATORY (AFCRL)

The logic network designer has suddenly found himself with a great wealth of new materials to work with. This happy situation has come about through a rapid and quiet revolution in microminiaturized components. Commonplace in the scientific and trade literature are the terms of this new technology: molecular electronics, integrated circuitry, planer and mesa transistors, thin film technology and so on. AFCRL, through contracts with a large number of companies -- Texas Instruments, Philco, RCA, Motorola -- and through its own in-house research has contributed to the rapidity of this advance.

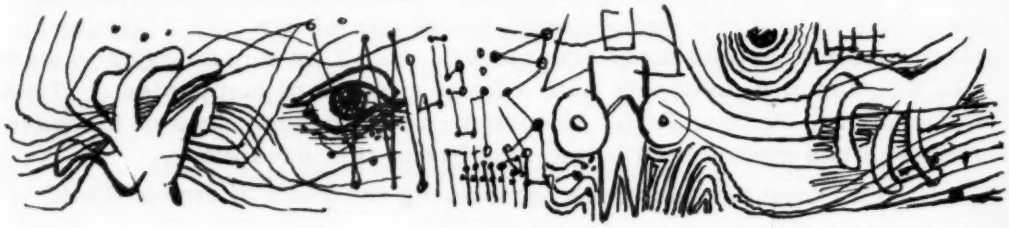
New computer networks performing the work of conventional

nets made up of resistors, capacitors and transistors can be reduced to microscopic sizes. The fabrication of hundreds or thousands of active devices in areas of only a few square inches is now feasible. These can be constructed fairly simply and economically, and this fact has given rise to a number of new computer concepts. Each of these microscopic elements by itself is likely to be unreliable, so this must be considered by the logic network designer. But this negative feature is more than offset by the fact that the small size and economy permits great redundancy. Through redundancy reliability is regained. Further, the designer can think increasingly in terms of parallel operation.

But when the designer attempts to fabricate the new networks, he finds that practical considerations stand in the way of making the essential tests and analysis of his networks that he would like to conduct. The microscopic size of these elements make it difficult to fabricate experimental circuitry for tests. A solution to this dilemma is to fabricate test elements from conventional transistors, resistors and capacitors in such a way as to simulate the operation of integrated circuitry.

AFCRL has designed several of these synthetic networks. One of these has great utility in considering logic networks using integrated techniques. Each element is connected to its neighbor elements with fixed physical connections but with provision for external control of electrical interconnections. The provision for a flexible means of rearranging interconnections once the unit is constructed, may represent a key advance toward future data processing devices.

External control of interconnections by photosensitive components permits the "rewiring" of computers for each specialized use. Many different data processing structures can thus be formed. In AFCRL's simulated network, interconnections are controlled by means of solar cells. Light is used to change an element from an active part of the net to simple conductors, in which case they are simply by-passed. Ultimately, bulky solar cells will be replaced by more sophisticated ways of controlling connections.



AFCRL notes

To learn more about lightning characteristics, AFCRL, several months ago, designed an experiment in which a long thin wire would be transported into a thunderhead. The wire would be carried aloft by a rocket. Lightning would be drawn down the wire, vaporizing it. In July, the first successful firings under the program were made when an AFCRL contractor launched two rockets from aboard a ship in the Caribbean. The rockets, trailing 1500 feet of wire, were launched in a 60 mile-an-hour squall. Each of the two lightning strokes were measured at 30,000 amperes. The wire down which the strokes were channelled was vaporized. This program is designed to learn more about the VLF electromagnetic signals generated by lightning strokes, and to investigate possible use of the ionized channel created by the vaporized wire as antenna for low frequency propagation. (Propagation Sciences Laboratory)

☆

Placed in operation in July by AFCRL is one of the most sensitive mass spectrometers commercially available. The spectrometer is the "Metropolitan Vickers MS-7," and is capable of detecting trace impurities as small as one part in a billion. The spectrometer will be used by AFCRL scientists for research on the ultrapurification of semiconductor materials. It operates only with solids. A sample rod of the material to be analyzed is vaporized by a high frequency spark. The vaporized material is accelerated through electrostatic and magnetic analyzers, which separate the elements in the vapor according to their relative masses. The resulting spectrum is recorded photographically for analysis. (Electronic Material Sciences Laboratory)

☆

A conference on the lunar environment, jointly sponsored by AFCRL and A.D. Little is planned for May 1963. Principal topics for the conference are: composition of lunar surface materials, shape and size of particles, microfeatures, soil mechanics, vacuum effects, radiation effects, micrometeoroid effects and effects on thermal properties. The conference, to be held in the Boston area, will be limited to a total attendance of 95. Dr. John W. Salisbury of AFCRL is co-chairman. (Research Instrumentation Laboratory)

modulation and detect

BERNARD S. MORGAN, JR., Captain, USAF, General Physics Division (AFOSR)

The optical spectrum from the infrared to the ultraviolet is one of the most fruitful areas of research today. This is especially true for the Air Force because of the potentialities of the uses of coherent light as an information carrier, in radar, in navigation systems and in data transfer in digital computers.

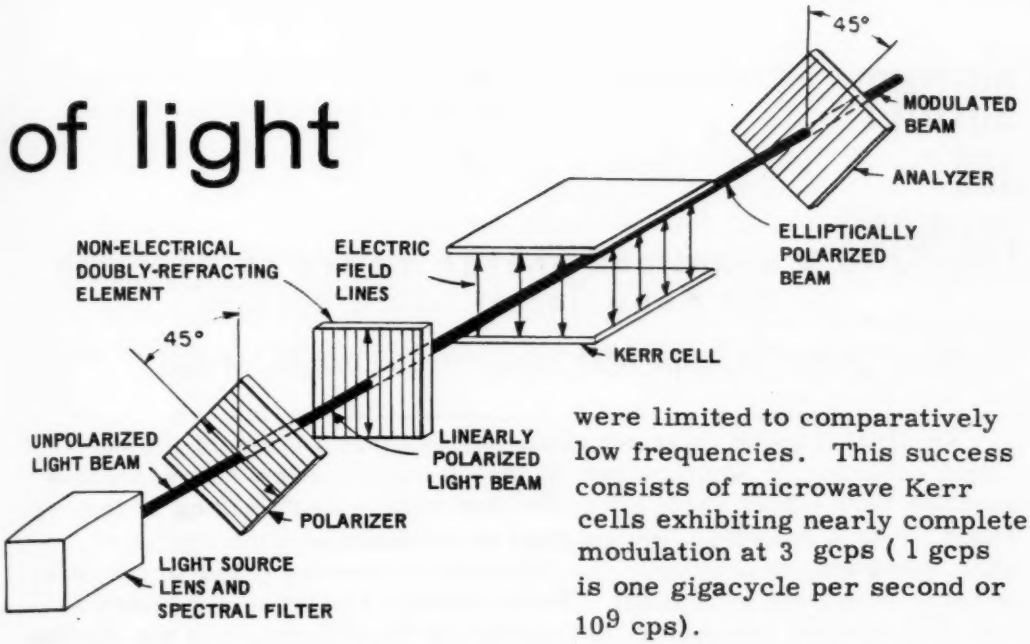
In the area of optical communications, the General Physics Division of AFOSR has been supporting basic research with Professor Don Holshouser at the University of Illinois on modulation and detection of light at microwave frequencies.

The problem of the production of very short pulses of light or light modulation has been studied for some time. Various schemes, many of which depend upon mechanical shutters, have been given to create shorter and shorter flashes of light. However, at frequencies above one megacycle per second the use of mechanical shutters for light control becomes prohibitively difficult. At these high frequencies electro- and magneto-optic effects, in which the propagation of light through a transparent medium is affected by the presence of an electric or magnetic field, offer much better means of high frequency light modulation. Of these, because of the relative ease of obtaining large rapidly changing electric fields compared to equivalent magnetic fields, the electro-optic Kerr Effect has proved more useful.

The Kerr Effect is the property of transparent media becoming doubly refracting when subjected to an intense electric field. This effect is observed in gases and liquids as well as in solids and it is due to a direct action of the electric field on the optical properties of the medium. Two condenser plates with a suitably chosen liquid between them constitute a Kerr cell. This cell in conjunction with two polarizing filters will operate as an optical shutter or light modulator when a varying electric potential is applied to the plates. Rapid changes in the electric field will thus produce a correspondingly rapid change in the intensity of the light beam passing through the apparatus.

Until the recent success of Professor Holshouser, Kerr cells

# of light



were limited to comparatively low frequencies. This success consists of microwave Kerr cells exhibiting nearly complete modulation at 3 gcps (1 gcps is one gigacycle per second or 10^9 cps).

The experimental study of methods of modulating light at microwave frequencies also requires good methods for the detection and measurement of such modulation. Professor Holshouser has recently reported success in the detection of modulated light by two different methods.

One method uses an interference technique in which light traverses a Kerr cell modulator twice, being reflected after the first transit by a movable mirror. The detecting element in this case is a conventional photomultiplier which measures the average light transmission. Since the average light transmission changes as the mirror is moved, the wavelength of the light modulation frequency can be obtained by merely measuring the distance between mirror positions which produce minimum transmission.

A second approach to the detection of light modulation is the realization of a fast-response photo detector. Since conventional photomultipliers cannot respond beyond about one gigacycle because of electron transit time problems, an entirely new approach was required. A successful solution was found in an electron multiplication process which is called dynamic crossed-field electron multiplication (DCFEM). Photomultipliers incorporating this process were fabricated which proved capable of detecting low-level microwave modulated light. This process has promise as a low-level, low noise detector of high-frequency modulated light, both in optical communications and as a basic research tool.

ROTONS and PHONONS

● quantized energy modes to describe the behavior of liquid helium

EDMUND P. GAINES, JR., Major, USAF, General Physics Division (AFOSR)

On first thought, it is not at all obvious that a study of the peculiar behavior of liquid helium in the vicinity of a few degrees above absolute zero (about -455°F) could lead to an understanding of factors which cause a smoothly flowing fluid to suddenly become turbulent. This, however, is precisely the objective of several projects currently being supported by AFOSR. These studies are being conducted at the University of Minnesota, University of Washington, and the Stevens Institute of Technology, under the respective directorships of Professors W. Zimmermann, G. J. Dash and Mr. L. Mead. The research is primarily concerned with the determination of energy distribution among various possible modes of molecular motion at these low temperatures. Liquid helium has been chosen for these studies because of two important facts.

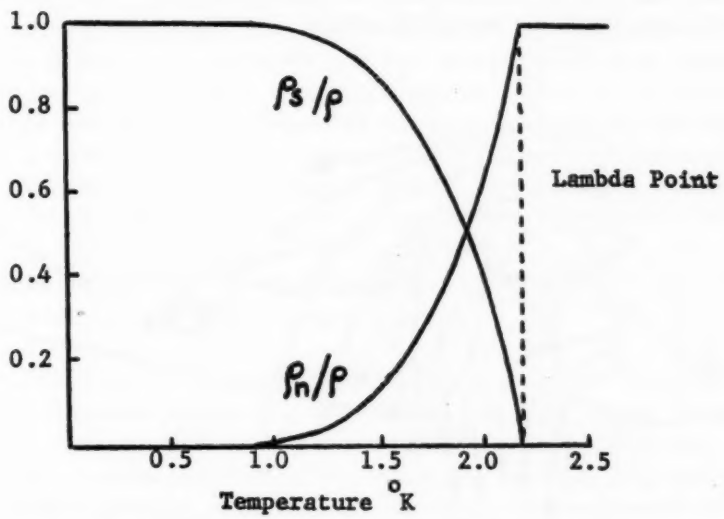
First, helium exhibits a curious property, known as the lambda phase transition, which occurs at a critical temperature near absolute zero. If the flow of liquid helium is observed as the temperature is steadily decreased, it exhibits all the characteristics of common fluids until its temperature reaches the phase transition point. At this temperature (known as the lambda phase transition temperature, or simply the lambda point), the flow rate begins suddenly to increase, indicating that the frictional influence of the walls of the containing channel has decreased. In other words, liquid helium at this temperature no longer exhibits the characteristics of normal fluids, because of the sudden decrease in its coefficient of viscosity. This decrease in viscosity is so dramatic that we are led to call liquid helium below the lambda point a superfluid.

In order to explain superfluidity, a two-component model was first proposed by Tisza in 1940 and later modified by Landau in 1941. This model assumes helium below the lambda temperature to be composed of two parts; one having the properties of a normal fluid and the other those of the superfluid. If the densities of these two

components are called ρ_n and ρ_s respectively, the net density is assumed given by their sum, or:

$$\rho = \rho_n + \rho_s.$$

An experiment to determine the relative contributions of the normal fluid and superfluid components to the over-all density was prepared by Andrionikashvili in 1946 with the results shown in the accompanying figure. From the curves of this diagram, it can be seen that the

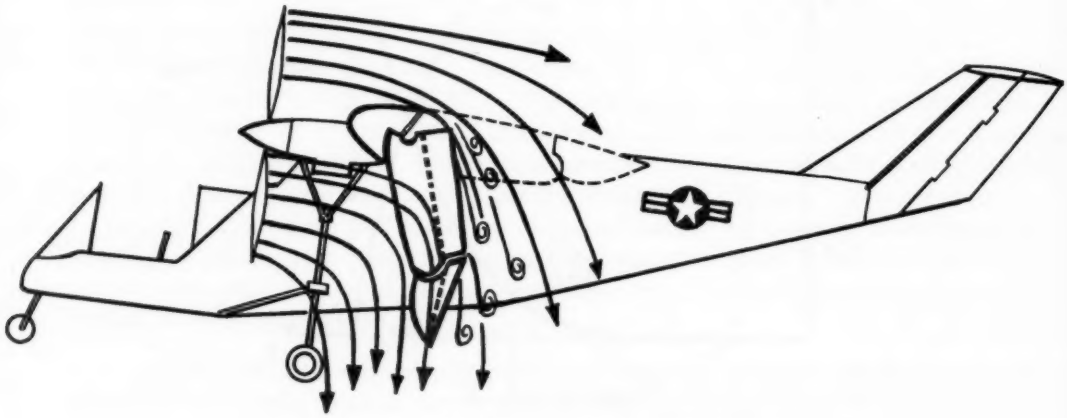


ADRIONIKASHVILI'S EXPERIMENT

contribution of the superfluid component increases very rapidly below approximately 2° Kelvin (zero degrees Kelvin is about -460°F). Furthermore, the two-fluid model mathematically leads to the possibility of two quantized modes of energy absorption. These modes, one longitudinal and the other rotational, are composed of elementary packets or quanta of energy called the phonon and roton, respectively. Energy in the form of phonons propagates as plane waves which result from excitation by heat. These waves are sometimes called second sound in analogy with the plane waves of acoustics. Energy in the form of rotons, on the other hand, does not propagate, but instead remains localized in the fluid in the form of tiny vortices. This latter action accounts for the superfluid characteristics of helium below the lambda temperature and is the important feature of these studies which may lead to a theory predicting the onset of

turbulence in fluid flow.

The second reason for conducting these studies using liquid helium arises from the fact that, at absolute zero, the orderliness of the fundamental "components" of matter becomes perfect. That is, all particle motion, in the classical thermodynamic sense, ceases. In other words, the usual translational and vibrational motions of the molecules and the attendant disorder of thermal motion disappears. This means that if a theory of turbulence (and also one for irreversible thermodynamic processes in general) can be developed, its consequences can be experimentally tested with greatest ease and accuracy at temperatures approaching absolute zero.



UNDERSTANDING IRREVERSIBLE THERMODYNAMICS WILL RESULT IN IMPROVED VTOL PERFORMANCE

The program being conducted by Mr. Mead is directed towards developing a more concise theory of turbulence, while those of Professors Zimmermann and Dash are directed towards experimental verification of the existence of the rotational modes predicted by the current two-component model of superfluid helium. If successful, these studies will aid greatly in the development of microscopic theories of turbulent flow and irreversible thermodynamics. These theories may lead to the more exact solution of many applied problems of vital interest to the Air Force. Examples of such problems are boundary control in high and low speed aerodynamics, prediction of the onset of cavitation in fluids, and more efficient design of reciprocating, turbine, and jet aircraft engines.

Superconductivity

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The technological implications of the phenomenon superconductivity, or the display of zero electrical resistivity in materials, have been known for many years. Their realization has not been achieved, however, until recent years for several reasons. First, it has only recently been possible to achieve the low temperatures at which superconductivity is displayed in a routine manner. Second, superconducting materials had to be developed in which moderate magnetic fields and current densities would not destroy the zero resistivity state. And third, the pehnomenon of superconductivity was not understood until the publication of the Bardeen, Cooper, Schrieffer theory of superconductivity. As a result we now find that superconducting materials are being used in electronic circuitry and for the production of moderately intense magnetic fields.

Before 1957, only a few laboratories in the world were actively concerned with superconducting materials. In that year, however, the publication of the theory of superconductivity by Bardeen, Cooper, and Schrieffer, commonly referred to as the BCS theory, gave a major impetus to experimental research in the area of superconductivity. Now almost every laboratory in the country has a research program on superconducting materials. The BCS theory has withstood this experimental attack, but it is generally accepted that refinements to the original theory are needed in order to explain the many detailed experimental facts.

The BCS theory postulates that electrons in a superconductor traveling in opposite directions and with oppositely-directed intrinsic angular momentum are coupled together with a pairing energy. In order to excite a single electron, either thermally or by means of an electric field, a non-infinitesimal amount of energy must be given to the electron. Many of the properties of superconductors can be explained in terms of this energy gap. Such properties include the specific heat, thermoconductivity, optical properties in the infrared, and the absorption of ultrasonic waves. All of these phenomena depend indirectly on this energy gap, and give an estimate of its width. It is

generally found to be of the order of magnitude of one millivolt.

Recently, however, Professor Ard of the University of Florida under contract AF49(638)-956, has measured this energy gap directly by means of electron tunneling experiments. Not only does this measure the gap width directly, but it also gives information on the number of electronic states as a function of energy.

The tunneling experiments were carried out as follows. A thin aluminum film is first evaporated onto a glass slide in a vacuum. This film is then allowed to oxidize for ten minutes at room temperature in air at reduced pressures. The film is then replaced in the vacuum system and another metal layer is evaporated onto the oxidized aluminum film. The latter film may be aluminum, lead, tin, or indium. Electrical contacts are then placed on each of these metal films and the current-voltage characteristics of this sandwiched structure is measured at liquid helium temperatures.

For small applied voltages, the current flowing through the thin insulating oxide layer is expected to be proportional to the applied voltage. This proportionality constant depends on the number of electronic states in each of the metal films and also on the relative probability of electrons occupying these states. This in turn depends on the applied voltages across the sandwiched structure, so that nonlinearity between the current and voltage might be expected. In particular, if the number of electronic states is zero, such as predicted for the energy gap region of a superconductor, one would expect no current to flow. Moreover, as the number of electronic states is predicted to decrease above the energy gap, we would expect to have a negative resistance region for this sandwiched structure.

By determining the negative resistance region and by studying the detailed temperature dependence of the current-voltage relationships of sandwiched films, Professor Ard has been able to determine directly the energy gap in superconducting materials and the number of electronic states as a function of energy. This direct measurement of the energy gap is found to agree within experimental error with the results of other indirect measurements, and the number of electronic states as a function of energy is found to agree qualitatively with the theoretical predictions of the BCS theory.

The growth of experimental evidence such as this tends to verify the validity of the BCS theory. Of more immediate importance to the

Air Force, however, is the fact that these sandwiched films display a negative resistance region.

Such a negative resistance region is one of the necessary requirements for the production of active, electronic devices. Such devices include amplifiers, oscillators, high-speed electronic switches, and memory storage elements.

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